CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

QUALITY ASSURANCE PROJECT PLAN (QAPP)

Concentrations of Pesticides in Sacramento Metropolitan Area Rainwater during the 2005 Orchard Dormant Spray Season

June 2005

State of California

California Environmental Protection Agency

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CENTRAL VALLEY REGION

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———

11020 Sun Center Drive #200
Rancho Cordova, CA 95670

———

Phone: (916) 464-3291

D I S C L A I M E R

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QUALITY ASSURANCE PROJECT PLAN (QAPP)

CONCENTRATIONS OF PESTICIDES IN SACRAMENTO METROPOLITAN AREA RAINWATER DURING THE 2005 ORCHARD DORMANT SPRAY SEASON

June 2005

REPORT PREPARED BY:

PETRA LEE
Environmental Scientist
Central Valley Regional Water Quality Control Board

GROUP A: PROJECT MANAGEMENT

1. TITLE AND APPROVAL SHEETS

APPROVAL SIGNATURES

California Department of Food and Agriculture Laboratory, Sacramento

Title:	Name:	Signature:	Date:
CDFA Quality Assurance Officer	Stephen Siegel		
Lab Manager	Dr. Mark Lee		

Central Valley Regional Water Quality Control Board

Title:	Name:	Signature:	Date:
Project Supervisor	Joe Karkoski		
Project Manager / CVRWQCB Acting QA Officer	Petra Lee		

2. TABLE OF CONTENTS

Page:

Group A: Project Management **4**
1. Title and Approval Sheets **4**
2. Table of Contents **5**
3. Distribution List **7**
4. Project/Task Organization **7**
5. Problem Definition/Background **9**
6. Project/Task Description **9**
7. Quality Objectives and Criteria for Measurement Data **12**
8. Special Training Needs/Certification **12**
9. Documents And Records **12**
Group B: Data Generation and Acquisition **14**
10. Sampling Process Design **14**
11. Sampling Methods **14**
12. Sample Handling and Custody **15**
13. Analytical Methods **17**
14. Quality Control **17**
15. Instrument/Equipment Testing, Inspection, and Maintenance **20**
16. Instrument/Equipment Calibration and Frequency **21**
17. Inspection/Acceptance of Supplies and Consumables **22**
18. Non-Direct Measurements (Existing Data) **22**
19. Data Management **22**
Group C: Assessment and Oversight **23**
20. Assessments & Response Actions **23**
21. Reports to Management **23**
Group D: Data Validation and Usability **24**
22. Data Review, Verification, and Validation Requirements **24**
23. Verification and Validation Methods **24**
24. Reconciliation with User Requirements **25**
25. Literature Cited **25**
APPENDIX 1. Sacramento Urban Rain Monitoring Standard Operating Procedure (SOP), 2005 ..... **26**
APPENDIX 2. Multi-Residue Method for Extraction and Analysis of Pesticides in Surface Water **33**
APPENDIX 3. Routine Operation and Maintenance of Buchi Rotary Evaporator **44**
APPENDIX 4. Routine Operation and Maintenance of Agilent /HP GC-MSD **49**

Table of Tables

Table 1. (Section 4) Personnel responsibilities. 7
Table 2. (Section 6) Project schedule timeline. 10
Table 3. (Section 7) Data quality objectives for laboratory measurements. 12
Table 4. (Section 9) Document and record retention, archival, and disposition information. 13
Table 5. (Section 11) Sampling locations and sampling methods. 15
Table 6. (Section 13) Laboratory analytical methods. 17
Table 7. (Section 14) Field Sampling QC. 19
Table 8. (Section 14) Analytical QC. 19
Table 9. (Section 15) Testing, inspection, maintenance of analytical instruments. 20
Table 10. (Section 16) Testing, inspection, maintenance of analytical instruments. 21
Table 11. (Section 17) Inspection/acceptance testing requirements for consumables and supplies. 22
Table 12. (Section 21) QA management reports. 23

Table of Figures

Figure 1. Organizational Chart……..8
Figure 2. Rainwater Monitoring Sites……..11
Figure 3. CVRWQCB Chain-of-Custody Form…….16

3. DISTRIBUTION LIST

Title:	Name:	Tel. No.:	QAPP No:
Regional Board Project Supervisor	Joe Karkoski	(916) 464-4668	
Regional Board Project Manager	Petra Lee	(916) 464-4603	
CDFA Quality Assurance Officer	Stephen Siegel	(916) 262-1434	
CDFA Lab Manager	Dr. Mark Lee	(916) 262-1434	
Deltakeeper Monitoring Coordinator	Kari Burr	(209) 464-6368	

4. PROJECT/TASK ORGANIZATION

4.1 Involved parties and roles.

The Central Valley Regional Water Quality Control Board (CVRWQCB) is responsible for implementing this project and for collecting rainwater samples at the Lincoln Airport site.

The California Department of Food and Agriculture's Center for Analytical Chemistry (CDFA Lab) will be the contract laboratory for all analyses. CDFA will analyze submitted samples in accordance with all laboratory method and quality assurance requirements found in this QAPP.

Deltakeeper will be responsible for rain sample collection at the Stockton site. Deltakeeper will also maintain and clean rain-collecting equipment, transfer samples to Regional Board staff through the proper Chain-of-Custody (COC) procedures, and take field notes when collecting samples.

Table 1. (Section 4) Personnel responsibilities.

Name	Organizational Affiliation	Title	Contact Information
Petra Lee	CVRWQCB	Project Manager and CVRWQCB Acting QA Officer	Ph: (916) 464-4603 Fax: (916) 464-4780 e-mail: plee@waterboards.ca.gov
Dr. Mark Lee	California Department of Food and Agriculture Center for Analytical Chemistry	Laboratory Manager	Ph: (916) 262-1434 Fax: (916) 262-1572 e-mail: mlee@cdfa.ca.gov
Stephen Siegel	California Department of Food and Agriculture Center for Analytical Chemistry	CDFA QA Officer	Ph: (916) 262-1434 Fax: (916) 262-1572 e-mail: ssiegel@cdfa.ca.gov
Kari Burr	Deltakeeper	Monitoring Coordinator	Ph: (209) 464-6368 Fax: (209) 464-5174 e-mail: kari@baykeeper.org

4.2 Quality Assurance Officer role.

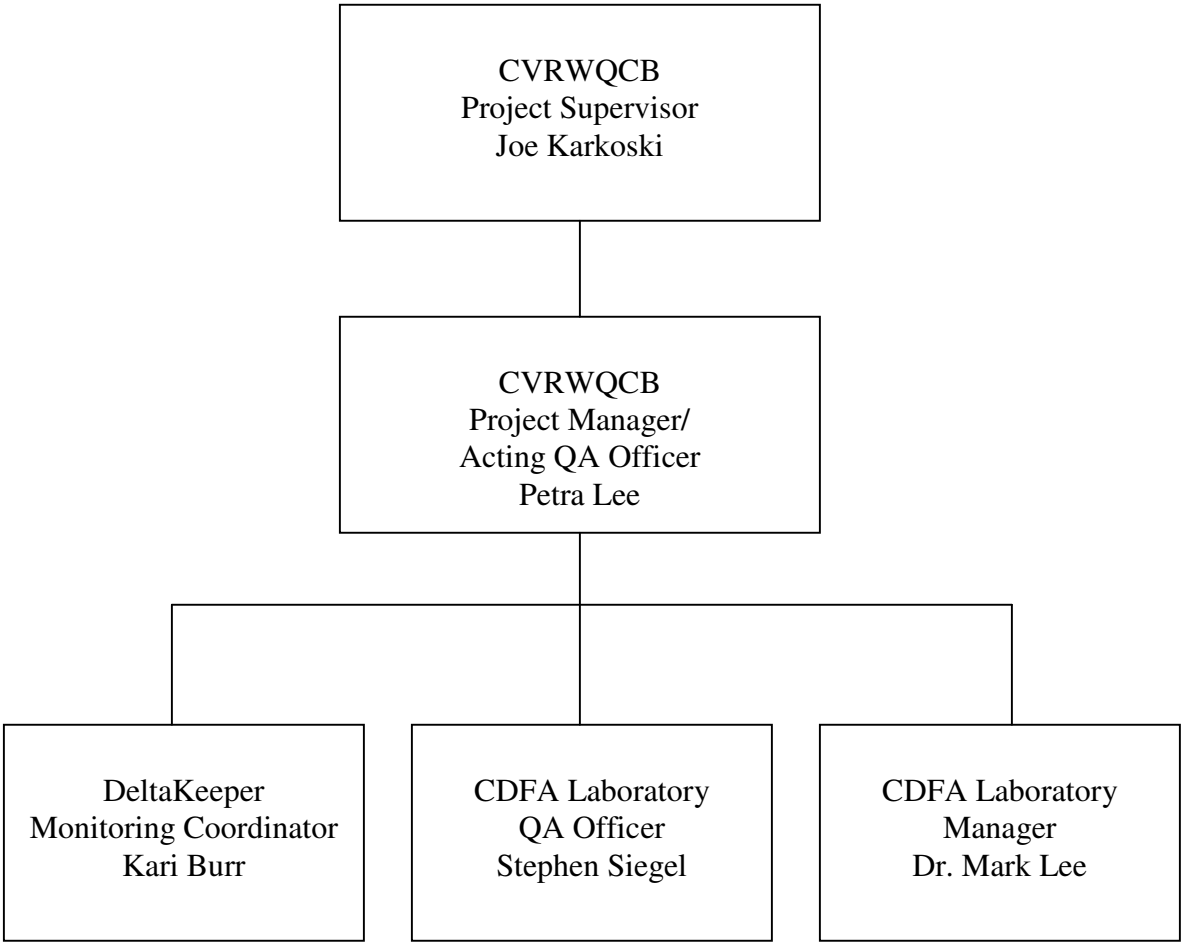
CVRWQCB does not currently have a Quality Assurance Officer and so Petra Lee will act as the QA officer for this project.

4.3 Persons responsible for QAPP update and maintenance.

The Project Manager, Petra Lee, will be responsible for changes and updates to this QAPP. Petra Lee will also be responsible for submitting drafts for review, preparing a final copy, and submitting the final QAPP for signatures.

4.4 Organizational chart and responsibilities

Figure 1. Organizational chart.



5. PROBLEM DEFINITION/BACKGROUND

Seven Sacramento County waterways are listed as impaired by diazinon and/or chlorpyrifos pursuant to Section 303(d) of the Clean Water Act. Because of this, the Central Valley Regional Water Quality Control Board (CVRWQCB) has conducted creek and rain monitoring during the orchard dormant spray season in 2001, 2002, 2003 (Spector *et al*, 2004) and 2004 (unpublished data). Rainwater was monitored since it is considered a potentially important pesticide transport mechanism and since the winter rainy season in the Sacramento Valley coincides with orchard dormant spray season. (Spector *et al,* 2004; Majewski and Baston, 2002; Bailey *et al*, 2000).

The rain monitoring results for sites in the Sacramento Valley in 2001-2003 have shown diazinon and chlorpyrifos concentrations in rainfall samples at elevated levels during the orchard dormant spray season. Pyrethoids were not detected at any of the 2002 or 2003 rain monitoring sites although carbaryl was detected at all rain monitoring sites in April 2003 (Spector *et al*, 2004). In order to further characterize and define the regional sources of diazinon, chlorpyrifos, and other organophosphate pesticides, rainwater samples will be collected in Placer County at the Lincoln Airport and in San Joaquin County in Stockton.

In addition to the monitoring conducted by Regional Board and Deltakeeper staff, the Sacramento Stormwater Permittees will be collecting rainwater at two sites in Sacramento County, at a rural site and a urban site. Results for the Sacramento County monitoring will be reported with the Regional Board's data in the Final Staff Report.

6. PROJECT/TASK DESCRIPTION

6.1 Work statement and produced products.

The main focus of this project will be on monitoring diazinon, chlorpyrifos and other organophosphate pesticide concentrations in rainfall in the Sacramento-Stockton area during and following the 2005 orchard dormant spray season. Information gained in this study will be used to augment the existing rainwater monitoring data collected from 2001-2003 (Spector *et al*, 2004) and 2004 (unpublished data) and to create a staff report of rain monitoring results for the 2005 orchard dormant spray season.

Rainwater samples will be collected at two locations at the northern and southern ends of an area spanning the greater Sacramento-Stockton metropolitan area. The northern site will be located in Placer County in Lincoln and the southern site will be located in San Joaquin County in Stockton. Both sites were part of previous rain-monitoring projects conducted in 2001, 2002, 2003, (Spector *et al*, 2004) and 2004 (unpublished data).

The two rain-monitoring sites in Placer and San Joaquin counties are:

Placer County:	Lincoln (R3) – Airport land use; commercial, residential, industrial land use on outskirts. The rain-monitoring site is located at the Lincoln Airport near the weather instruments, east of the buildings on 1420 Flightline Drive.
San Joaquin County:	Near Stockton (R4) – Urbanized land. The rain-monitoring site is located at 3536 Rainier in Stockton.

Rain samples will be collected at these sites following up to ten storm events from February through April 2005. Samples will be analyzed for diazinon, chlorpyrifos, and other selected pesticides (listed in table 7) by the CDFA Lab in Sacramento, California.

6.2. Constituents to be monitored and measurement techniques.

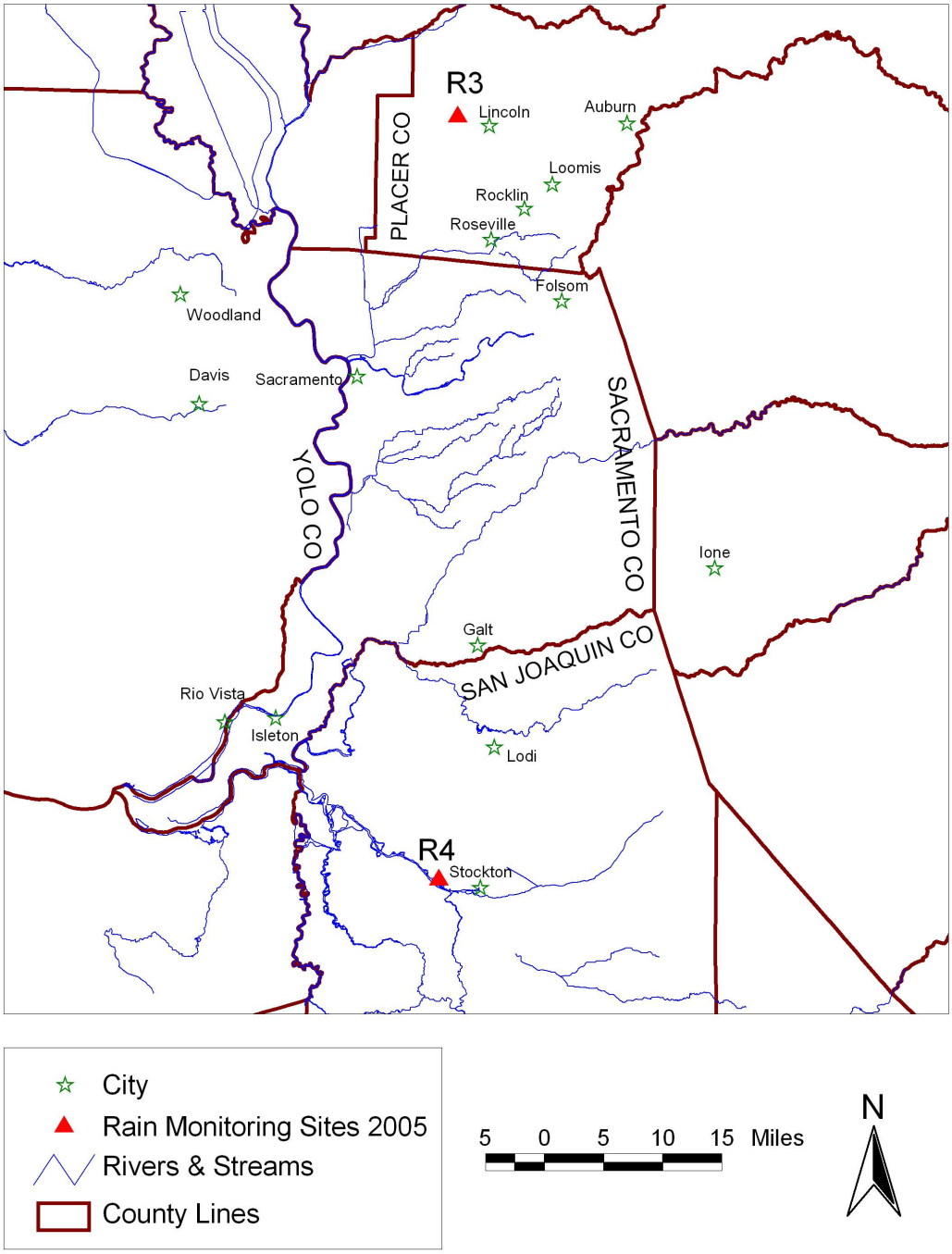
Concentrations of diazinon, chlorpyrifos and other organophosphate pesticides will be determined using gas chromatography mass spectrometry (GC/MS). A description of the method is attached (Appendix 2).

6.3 Project schedule

Table 2. (Section 6) Project schedule timeline.

Activity	Date		Deliverable	Deliverable Due Date
	Anticipated Date of Initiation	Anticipated Date of Completion		
Sample Collection in Lincoln	2/2005	4/2005	Sample concentration data	Within 4 weeks of sample delivery
Sample Collection in Stockton	2/2005	4/2005	Sample concentration data	Within 4 weeks of sample delivery
Summarize Data	4/2005	6/2005	Complete data set	6/2005
Draft Report	6/2005	9/2005	Draft report for review	9/2005
Final Report	9/2005	10/2005	Final report	10/2005

Figure 2. Rainwater monitoring sites.



6.5 Project Constraints

Sample collection will be limited to the Sacramento Valley's rainy season and samples will only be collected during and after the orchard dormant spray season. Because of time and storm event limitations, sampling for 10 storm events may not occur.

7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

Table 3. (Section 7) Data quality objectives for laboratory measurements.

Group	Parameter	Accuracy	Precision	Recovery	Target Reporting Limits	Completeness
Organophosphate pesticides	Diazinon	Standard Reference Materials (diazinon) within 95% CI** stated by provider of material.	Field replicate or MS/MSD ± 25% RPD*.	Matrix spike within 70%-130%	0.020 ppb	90%
Organophosphate pesticides	Chlorpyrifos	Standard Reference Materials (chlorpyrifos) within 95% CI** stated by provider of material.	Field replicate or MS/MSD ± 25% RPD.	Matrix spike within 70%-140%	0.010 ppb	90%

*RPD – Relative Percent Difference
**CI – Confidence Interval

8. SPECIAL TRAINING NEEDS/CERTIFICATION

8.1 Specialized training or certifications.

No special training or certification is necessary other than a familiarity with the Standard Operating Procedure (SOP) found in Appendix 1.

9. DOCUMENTS AND RECORDS

The sampling crew will collect the rainwater samples and provide the CDFA Lab with the complete and signed original Chain-of-Custody (COC) forms upon delivering the samples to the lab. A copy of the completed and signed COC will be obtained from CDFA lab staff when samples are delivered to the lab. Sampling crews are required to take field notes at each of the two monitoring sites and ensure that copies of the COC and field notes are provided to the Project Manager after each sampling day.

The CVRWQCB Project Manager will ensure that copies of this QAPP will be distributed to all parties involved with the project, including sampling crew members. Copies will be sent to the CDFA Manager for distribution within the CDFA. Any future amended QAPPs will be distributed in the same fashion. The most current QAPP will be held at the CVRWQCB.

Persons responsible for maintaining records for this project are as follows. CVRWQCB Project Manager, Petra Lee, will maintain all sample collection, sample transport, chain-of-custody, and field analyses forms, as well as the database. Stephen Siegel, CDFA laboratory manager will maintain all records associated with the receipt and analysis of samples analyzed for organophosphate pesticides. Petra Lee will arbitrate any issues relative to records retention and any decisions to discard records.

All records and lab reports will be passed to the Regional Board Project Manager, Petra Lee, at project completion. Copies of the records will be maintained at CVRWQCB and CDFA for five years after project completion then discarded, except for the database, which will be maintained.

Table 4. (Section 9) Document and record retention, archival, and disposition information.

	Identify Type Needed	Retention	Archival	Disposition
Sample Collection Records	Chain-of-Custody	Original with CDFA Lab	Copies with CVRWQCB	Copy stored at Regional Board for at least 5 years
Field Records	Field Notes	Petra Lee	Original with CVRWQCB	Stored at Regional Board for at least 5 years
Analytical Records	Excel Sample Reports	CDFA	Copies with CVRWQCB	Stored at Regional Board for at least 5 years
Data Records	Excel Database	Original with CVRWQCB	Stored on Regional Board Computer Server	Stored at Regional Board for at least 5 years
Assessment Records	Draft and Final Staff Report	Original with CVRWQCB	Regional Board Library, Posted on Regional Board Website	Stored Permanently at Regional Board

GROUP B: DATA GENERATION AND ACQUISITION

10. SAMPLING PROCESS DESIGN

Sampling sites were chosen on a north-south axis in and around the Sacramento area with the Lincoln site being the northernmost site and Stockton site being the southernmost site. Two sample sites are being monitored between the northernmost and southernmost sites by the Sacramento Urban Stormwater Permittees and are located within the Sacramento area. One site is in the Sacramento urban area at Sump 104 and one site is within the rural Sacramento area located at the Prairie City State Vehicular Recreation Area. Samples will be collected at all four sites from February to April 2005, during and after the orchard dormant spray season.

The rain sampling protocol is based on Regional Board sampling techniques employed during Sacramento metropolitan area rain monitoring from 2001-2003 (Spector *et al*, 2004) and in 2004 (unpublished data). Sampling methods and protocol, and lab analyses are described in the Standard Operating Procedure (Appendix 1) and in the next section (Section 11). Sampling areas are described in more detail in Section 6 of this document. More information on past rain monitoring can be found in Spector *et al* (2004).

11. SAMPLING METHODS

Sampling methods are included in more detail in the Standard Operating Procedure (SOP) in Appendix 1. A brief narrative of the sampling methods is included below.

During the 2005 orchard dormant spray season, which begins in early-to mid-January and continues for approximately six weeks, rain sample collecting will be conducted for five rain events. Following the 2005 orchard dormant spray season (starting in approximately mid-March), rain samples will be collected for up to five rain events, weather permitting. The two sampling periods may run together if fewer than 5 storms occur during the orchard dormant spray season.

The rain sampling protocol is based on the Regional Board's sampling techniques employed during Sacramento metropolitan area rain monitoring in 2001 through 2004 (Spector *et al*, 2004 and unpublished data). Rainfall samples will be collected using rainfall sampling devices that consist of a 19-inch diameter stainless steel bowl with a hole punched in the bottom and secured with stainless steel wire to the top of a 5-gallon plastic bucket. A 3/8-inch diameter piece of stainless steel tubing set into the hole in the bowl will guide the water into a 2.5-gallon glass carboy set inside the bucket underneath the bowl.

When possible, all surfaces of the rain sampling devices that will come into contact with the rainwater samples, including the glass carboys, will be cleaned with Alconox or Liquinox in the Regional Board laboratory or at the Deltakeeper premises prior to sampling. If a Liquinox cleaning is not possible, the rain sampling devices will be rinsed three times with deionized water in the field.

An attempt will be made to deploy the rain collectors as close as possible to the beginning of anticipated storm events, generally a day before the forecasted storm event. Sample collecting devices will be deployed when 0.25 inches of rain are forecasted in order to collect a sufficient amount of rain. If enough rainfall is not collected within 24 hours, the collectors will be left in place to collect a sufficient amount of rainfall (approximately 1-liter). If the storm continues for multiple days with over 0.25 inches of rain, a sample will be collected for each 0.25 inches of rain or every 24 hours (whichever occurs later) throughout the storm event.

Once collected, the rain samples will be poured into 1-liter (L) glass amber bottles. The bottles will first be rinsed three times with sample water before being filled with the sample. The sample bottles and any included QA/QC bottles will be labeled, placed into a cooler with ice and delivered to the CDFA Lab in Sacramento, California under chain-of-custody protocol for analysis.

Any problems with lab procedures and protocol will be addressed by the CDFA Lab QA Officer, Steven Siegel. Any other problems will be addressed and resolved by the Regional Board Project Manager, Petra Lee. Any deviations will be documented in the Final Staff Report only if it affects the interpretation of the laboratory results, otherwise the deviation will be documented and held with the field sheets and copies of the COC's, by the Regional Board.

Table 5. (Section 11) Sampling locations and sampling methods.

Sampling Location	Location ID #	Matrix	Analytical Parameter	# Samples (including field duplicates)	Containers #, size, type	Preservation	Maximum Holding Time:
Lincoln Airport	R3	Rainwater	Organo-phosphate pesticides	Up to 12	1L Amber glass bottle, Fisher Scientific 300 series	Ice (~4°C)	7 Days
Stockton	R4	Rainwater	Organo-phosphate pesticides	Up to 12	1L Amber glass bottle, Fisher Scientific 300 series	Ice (~4°C)	7 Days

12. SAMPLE HANDLING AND CUSTODY

The sample handling and custody is described in more detail in the Standard Operating Procedures (SOP) in Appendix 1, but the following is a brief summary.

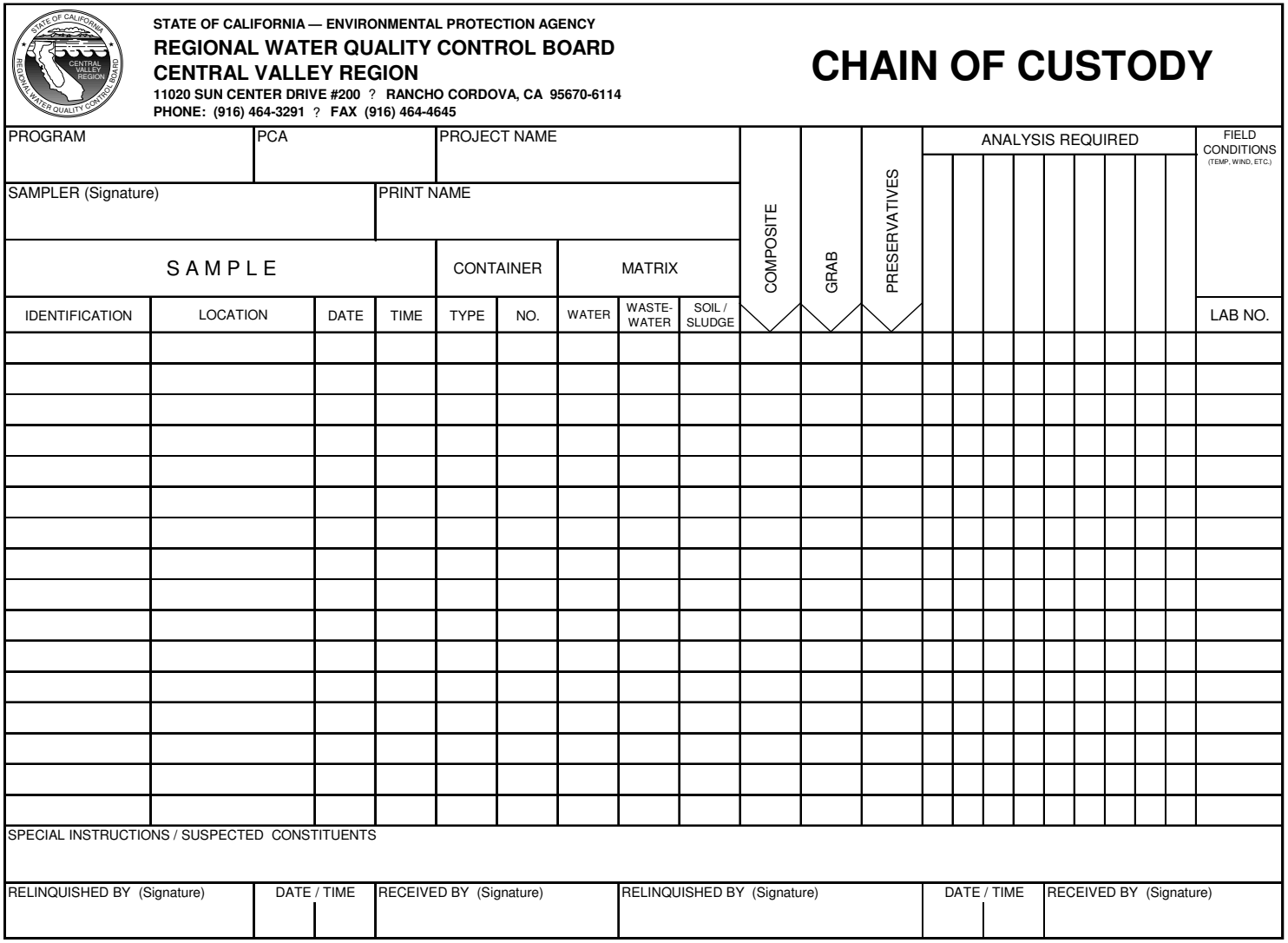
Samples will be collected in Fisher Scientific 300 Series certified pre-cleaned 1L amber glass bottles that will be labeled according to the SOP and placed into foam sleeves. In the field, samples will be placed with ice into an ice chest to be delivered to the lab by CVRWQCB staff on the collection day or on the following business day. If delivery is postponed until the next business day, samples will be held in a secure area until being transported to the lab. Extraction must be completed within seven days of the collection date and samples must be stored in the dark at 4°C until the extraction.

Sampling crews will provide the CDFA Lab with the completed and signed original chain-of-custody (COC) forms upon delivering the samples to the lab. A copy of the completed and signed COC will be obtained from CDFA lab staff when samples are delivered to the lab. Sampling crews are required to take field notes at both of the monitoring sites using a blank field sheet form, and to ensure that copies of the COC and the field notes are provided to the Project Manager after each sampling day.

Samples may be disposed of when analysis is completed and all analytical quality assurance/quality control procedures are reviewed and accepted.

A copy of the chain-of-custody form is located on the following page.

Figure 3. CVRWQCB Chain-of-Custody Form



STATE OF CALIFORNIA — ENVIRONMENTAL PROTECTION AGENCY
REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION
11020 SUN CENTER DRIVE #200 ? RANCHO CORDOVA, CA 95670-6114
PHONE: (916) 464-3291 ? FAX (916) 464-4645

CHAIN OF CUSTODY

PROGRAM	PCA	PROJECT NAME
SAMPLER (Signature)	PRINT NAME	

SAMPLE				CONTAINER		MATRIX			COMPOSITE	GRAB	PRESERVATIVES	ANALYSIS REQUIRED									FIELD CONDITIONS (TEMP, WIND, ETC.)
IDENTIFICATION	LOCATION	DATE	TIME	TYPE	NO.	WATER	WASTE-WATER	SOIL / SLUDGE													LAB NO.

SPECIAL INSTRUCTIONS / SUSPECTED CONSTITUENTS

RELINQUISHED BY (Signature)	DATE / TIME	RECEIVED BY (Signature)	RELINQUISHED BY (Signature)	DATE / TIME	RECEIVED BY (Signature)

13. ANALYTICAL METHODS

The procedure for CDFA lab's *Multi-Residue Method for Extraction and Analysis* is included in Appendix 2. The CDFA laboratory analytical methods are briefly outlined in the table below.

Table 6. (Section 13) Laboratory analytical methods.

Analyte	Project Quantitation Limit (µg/L)**	Achievable Laboratory Limits, MDL* (µg/L)
Diazinon	0.020	0.007
Chlorpyrifos	0.010	0.004
Eptam (EPTC)	0.050	0.020
Simazine	0.200	0.005
Carbaryl	0.020	0.007
Metolachlor	0.020	0.007
Cyanazine	0.050	0.007
Dacthal (DCPA)	0.050	0.007
Methidathion	0.030	0.010
Propargite	0.500	0.150
Azinphos-methyl	0.050	0.007

*MDL – Method Detection Limit
**µg/L = micrograms/liter

14. QUALITY CONTROL

Internal quality control (QC) is achieved by analyzing a series of duplicate, blank, spike, and spike duplicate samples to ensure that analytical results meet the specified QC objectives. The QC sample results are used to quantify precision and accuracy and identify any problem or limitation in the associated sample results.

Field Quality Control

Field QC samples are used to assess the influence of sampling procedures and equipment used in sampling. They are also used to characterize matrix heterogeneity. For basic water quality analyses, quality control samples to be prepared in the field will consist of field equipment blanks and field duplicates.

Field Duplicates

The purpose of analyzing field duplicates is to demonstrate the precision of sampling and analytical processes. Field duplicates will be prepared at the rate of one per sampling season and analyzed along with the associated environmental samples. Field duplicates will consist of two aliquots from the same sample. If a relative percent difference (RPD) greater than 25% is confirmed by reanalysis, environmental results will be qualified as estimated. The sampling personnel should be notified so that the source of sampling variability can be identified (if possible) and corrective measures taken prior to

the next sampling event. Field duplicates are collected according to the Sacramento Urban Rain Monitoring Standard Operating Procedure, 2005 (Appendix 1).

Field Equipment Blanks

The purpose of analyzing field equipment blanks is to demonstrate that field sampling equipment is free from contamination. These will be prepared and analyzed at a rate of two per sampling season; one equipment blank will be collected after laboratory cleaning and one equipment blank will be collected after field cleaning of the sampling equipment. Details about collection of field equipment blanks are included in the Sacramento Urban Rain Monitoring Standard Operating Procedure, 2005 in Appendix 1. The blanks will be analyzed using the same analytical methods specified for environmental samples. If any analytes of interest are detected at levels greater than the limit of detection (LOD), the source(s) of contamination should be identified and corrected, the affected equipment should be re-cleaned, and new equipment blanks should be prepared and analyzed. Samples collected previous to the affected field equipment blank will be noted for possible contamination.

Laboratory Quality Control

Laboratory QC is necessary to control the analytical process within method and project specifications and to assess the accuracy and precision of analytical results. For basic water quality analyses, quality control samples prepared in the CDFA laboratory will consist of lab blanks, matrix spikes, and matrix spike duplicates. Laboratory spikes, internal standards, and a surrogate will be added to each sample. The surrogate will be chlorpyrifos methyl and the matrix spike and matrix spike duplicate will be spiked with diazinon and chlorpyrifos. Known amounts of internal standards are added to extracted samples to ensure that if evaporation occurs, results will still be quantifiable. See table 9 for a synopsis of laboratory QA/QC procedures.

Blanks

The purpose of analyzing lab blanks is to demonstrate that the analytical procedures do not result in sample contamination. Lab blanks will consist of laboratory-prepared blank water spiked with the surrogate and processed along with the batch of environmental samples.

Instrument blanks are run in order to determine whether the instrumentation is causing any contamination of the samples. The instrument blank consists of pure water spiked with surrogate.

If the result for any lab or instrument blank is greater than the limit of detection, the source(s) of contamination should be corrected and the associated samples should be reanalyzed. If reanalysis is not possible, the associated sample results should be qualified as below detection at the reported blank value.

Spikes

The purpose of analyzing matrix spikes and matrix spike duplicates is to demonstrate the performance of the analytical method in a particular sample matrix. One 1-L sample will be collected and split, then analyzed as a matrix spike sample and a matrix spike duplicate sample. Each matrix spike and matrix spike duplicate will consist of an aliquot of laboratory-spiked environmental sample; the spike will consist of the surrogate, chlorpyrifos methyl, and diazinon and chlorpyrifos.

The purpose of analyzing laboratory spikes is to demonstrate the accuracy of the analytical method. Laboratory spikes will be analyzed at the rate of one per sample batch. Laboratory spikes will consist of laboratory blank water fortified with the surrogate, chlorpyrifos methyl, and with diazinon and chlorpyrifos.

If recovery of any analyte is outside the acceptable range for accuracy, the analytical process is not being performed adequately for that analyte. In this case, if the matrix spikes are also outside the acceptable range, the lab spike and associated samples should be reanalyzed. If reanalysis is not possible, the associated sample results should be qualified as low or high biased.

Matrix spike concentrations will be added at five to ten times the reporting limit for the analyte of interest. If matrix spike recovery of any analyte is outside the acceptable range, the results for that analyte have failed the acceptance criteria. If recovery of the laboratory spike is acceptable, the analytical process is being performed adequately for that analyte, and the problem is attributable to the sample matrix. An attempt should be made to correct the problem (by dilution) and re-analyze

the samples and the matrix spikes. If the matrix problem cannot be corrected, the results for that analyte will be qualified as appropriate (low or high biased) due to matrix interference. If the matrix spike duplicate RPD for any analyte is greater than the precision criterion, the results for that analyte have failed the acceptance criteria. If the RPD for laboratory duplicates is acceptable, the analytical process is being performed adequately for that analyte, and the problem is attributable to the sample matrix. An attempt should be made to correct the problem (by dilution, concentration, etc.) and re-analyze the samples and the matrix spike duplicates. If the matrix problem cannot be corrected, the results will be qualified for that analyte as not reproducible, due to matrix interference.

Table 7. (Section 14) Field Sampling QC.

Matrix: Water
Sampling SOP: Appendix 1
Analytical Parameter(s): Organophosphate pesticides
Analytical Method/SOP Reference: Appendix 1
Sample locations: 2

Field QC	Frequency/Number per sampling event	Acceptance Limits
Field Equipment Blanks	2 per sampling season	Less than Limit of Quantification
Field Duplicate	2 per sampling season	RPD ≤ 25%
Cooler Temperature	Measured by analyzing lab at time of delivery	≤ 4°C

Table 8. (Section 14) Analytical QC.

Matrix: Water
Sampling SOP: Appendix 2
Analytical Parameter(s): Organophosphate pesticides
Analytical Method/SOP Reference: Appendix 2
Sample locations: 2

Laboratory QC	Frequency/Number	Acceptance Limits
Lab Blank	1/batch	80-125% for surrogate All target analytes below reporting limit
Instrument Blank	After any standards	All target analytes below reporting limit
Matrix Spike	1 per sampling season	70-130 % diazinon; 70-140% chlorpyrifos
Matrix Spike Duplicate	1 per sampling season	70-130 % diazinon; 70-140% chlorpyrifos RPD ≤ 25%
Lab Spike	1/batch	80-125% for surrogate 70-130 % diazinon; 70-140% chlorpyrifos
Surrogate (Chlorpyrifos methyl)	All samples and standards	80-125% for surrogate
Internal Standards	All samples and standards	50-200%

15. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

A visual inspection of the field equipment will be done to detect visible contamination of the collector, tears in the bag holding the equipment, and contamination of the sampling bottles.

Table 9. (Section 15) Testing, inspection, maintenance of analytical instruments.

Equipment / Instrument	Maintenance Activity, Testing Activity or Inspection Activity	Responsible Person	Frequency	SOP Reference
Buchi rotary evaporator	Rinsing condenser	CDFA Chemists	Before each sample	Appendix 3
6890/5973MSD	Injector cleaning	CDFA Chemists	As needed	Appendix 4

16. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

No calibration is necessary for field equipment. Laboratory calibrations are briefly described below and in more detail in Appendix 2, *Multi-Residue Method for Extraction and Analysis of Pesticides in Surface Water.*

Lab Method Calibration
Five levels of standards are prepared in a matrix of organic-free reagent grade water to calibrate the analysis method. A linear regression is used including 0,0. The R-squared value should be greater or equal to 0.99. Standards are run with the sample set to check for calibration integrity. Continuing calibration standard values should be within ±25% of calibration. Residue concentration is taken from instrument report table and calculated. If the residue amount falls outside the calibration curve, the sample will be diluted and reanalyzed.

$$\text{Residue Amt (ppt)} = \frac{\left(\text{Instrument amt} \times 500\text{g}\right)}{\text{Weight of sample}}$$

If R-squared value of the calibration curve is <0.99, the pesticide level may be determined by direct comparison of residue response to the average response of the nearest bracketing standard concentration. Response of bracketing standards should not vary more than 25%. The residue response should fall within ±30% of standard response. If the residue amount falls outside calibration curve, the sample will be diluted and reanalyzed. A non-linear calibration may be necessary to achieve low detection limits or address specific instrumental techniques. Non-linear calibration is not to be used to compensate for detector saturation or to avoid instrument maintenance.

Calculation using single point comparisons:

$$\text{Sample amt (ppt)} = \left(\frac{\text{Sample response}}{\text{Avg response of bracketing stds}}\right) \times \left(\frac{500\text{g}}{\text{Weight of sample (g)}}\right) \times \text{Std amt}$$

Table 10. (Section 16) Testing, inspection, maintenance of analytical instruments.

Instrument	SOP reference	Calibration Description and Criteria	Frequency of Calibration	Responsible Person
6890/5973M SD	Appendix 2	5-point initial calibration	Beginning of each analytical run	CDFA Chemist

17. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Gloves, sample containers, and any other consumable equipment used for sampling will be inspected by the sampling crew on receipt and will be rejected/returned if any obvious signs of contamination (torn packages, etc.) are observed. Inspection protocols and acceptance criteria for laboratory analytical reagents and other consumables are documented in the CDFA Quality Manual (Cusick, 2004). The laboratory QA manual is available for review at the CDFA laboratory.

Table 11. (Section 17) Inspection/acceptance testing requirements for consumables and supplies.

Project-Related Supplies / Consumables	Inspection / Testing Specifications	Acceptance Criteria	Frequency	Responsible Individual
Organic-free Reagent Water	Lab Blank	No target analytes above Reporting Limit	1/batch	CDFA Chemist
Methylene chloride	Lab Spike	No target analytes above Reporting Limit	1/batch	CDFA Chemist
Na_2SO_4	Lab Blank	No target analytes above Reporting Limit	1/batch	CDFA Chemist
NaCl	Lab Blank	No target analytes above Reporting Limit	1/batch	CDFA Chemist

18. NON-DIRECT MEASUREMENTS (EXISTING DATA)

The only non-direct measurements are previous data and information from earlier studies (Spector *et al*, 2004 and unpublished data) which be used as a comparison to the current data.

19. DATA MANAGEMENT

Data will be maintained as established in section 9 above. Copies of field logs, copies of chain-of-custody forms, original preliminary and final lab reports and electronic media reports will be stored with the Regional Board Project Manager. An electronic copy of data will be put into a permanent database at the CVRWQCB by the Project Manager. All field logs will be relinquished to the Project Manager. The CDFA Lab will retain the original chain-of-custody forms and copies of the preliminary and final data reports.

GROUP C: ASSESSMENT AND OVERSIGHT

20. ASSESSMENTS & RESPONSE ACTIONS

Quality assurance/quality control will be maintained as described in Section 14 and QA/QC procedures are briefly outlined in Table 9. Blanks will be used to check for contamination of equipment. Equipment blanks are used to check for contamination of field equipment and instrument blanks are used to check for contamination of laboratory equipment. If the result for a single lab or instrument blank is greater than the acceptance limits the source(s) of contamination will be corrected and the associated samples should be reanalyzed. If reanalysis is not possible, the associated sample results should be qualified as below detection at the reported blank value.

Spikes will be used to check for recovery rates of the surrogate, chlorpyrifos methyl, and for the recovery of chlorpyrifos and diazinon in the sample matrix and in pure water. All samples will be spiked with the surrogate. Known amounts of internal standards are added to extracted samples to ensure that if evaporation occurs, results will still be quantifiable. If recovery of any analyte is outside the acceptable range for accuracy, the analytical process is not being performed adequately for that analyte. In this case, if the matrix spikes are also outside the acceptable range, the lab spike and associated samples should be reanalyzed. If reanalysis is not possible, the associated sample results should be qualified as low or high biased.

The CVRWQCB Project Manager will make periodic assessments of the sampler's/sampling team's methods. Steps will be made to assure that the sampler/sampling team is sampling and maintaining sampling equipment in a manner consistent with the standard operating procedures. The CDFA QA Officer will make periodic assessments of CDFA methods.

Data will be maintained as established in Section 9 above. Copies of field logs, copies of chain-of-custody forms, original preliminary and final lab reports, and electronic media reports will be sent to the Regional Board Project Manager. The Project Manager will also maintain the original field sheets, copies of the chain-of-custodies and the database. The CDFA Lab will retain the original chain-of-custody forms.

21. REPORTS TO MANAGEMENT

Draft and final reports will be issued by CVRWQCB according to the following table.

Table 12. (Section 21) QA management reports.

Type of Report	Frequency	Projected Delivery Dates	Person(s) Responsible for Report Preparation	Report Recipients
Complete data set and summary	one time only	5/2005	Petra Lee	Acting CVRWQCB QA Officer Petra Lee
Draft report for review	one time only	9/2005	Petra Lee	Project Supervisor Joe Karkoski
Final report	one time only	10/2005	Petra Lee	CVRWQCB Public Website
Statistical analysis of lab QC's	one time only	5/2005	Stephen Siegel	CVRWQCB Project Manager

GROUP D: DATA VALIDATION AND USABILITY

22. DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

Data generated by project activities will be reviewed against the data quality objectives cited in Section 7 and the quality assurance/quality control practices cited in sections 14, 15, 16, and 17. Data will be separated into three categories: data meeting all data quality objectives; data failing precision or recovery criteria; and data failing to meet accuracy criteria. Data meeting all data quality objectives, but with failures of quality assurance/quality control practices will be set aside until the impact of the failure on data quality is determined. Once determined, the data will be moved into either the first category or the last category.

Data falling in the first category is considered usable by the project. Data falling in the last category is considered not usable. Data falling in the second category will have all aspects assessed. If sufficient evidence is found supporting data quality for use in this project, the data will be moved to the first category, but will be flagged with a "J" as per EPA specifications (USEPA, 2004).

In cases where field blank results exceed the acceptance criteria, the associated sample results will be qualified and reported as follows:

- Measured environmental sample concentrations greater than or equal to 5 times the field blank level will be reported with no qualification.
- Measured environmental sample concentrations less than 5 times the field blank level will be qualified as "less than" the measured value, e.g. if a field blank is equal to 1.5 µg/L, a measured environmental concentration of 4.0 µg/L will be reported as <4.0 µg/L.
- Any data qualifications resulting from QC analyses will be reported with the environmental data as appropriate.

Data will also be compared against similarly collected data from previous studies (Spector *et al*, 2004 and unpublished data) to determine reasonability of the data set.

23. VERIFICATION AND VALIDATION METHODS

Laboratory Data Review, Verification and Reporting

The CDFA QA Officer, Stephen Siegel, will use this QAPP for validating the data generated by the laboratory. The laboratory personnel will verify that the measurement process was "in control" (i.e., all specified data quality objectives were met or acceptable deviations explained) for each batch of samples before proceeding with analysis of a subsequent batch. In addition, the CDFA laboratory will establish a system for detecting and reducing transcription and/or calculation errors prior to reporting data.

The laboratory analyst performing the analyses is responsible for the reduction of the raw data generated at the laboratory bench to calculate the concentrations.

The analytical process includes verification or a quality assurance review of the data. This includes:

- Verifying the calibration samples for compliance with the laboratory and project criteria;
- Verifying that the batch QC were analyzed at a proper frequency and the results were within specifications;
- Comparing the raw data with reported concentration for accuracy and consistency;
- Verifying that the holding times were met and that the reporting units and quantitation limits are correct;
- Determining whether corrective action was performed and control was re-established and documented prior to reanalysis of QC or project samples;
- Verifying that all project and QC sample results were properly reported and flagged; and
- Preparing batch narratives that adequately identify and discuss any problems encountered.

Specific Quality Control procedures are documented in the laboratory quality assurance manual (Cusick, 2004). After the data have been reviewed and verified, the laboratory reports are signed for release and distributions. Raw data and supporting documentation are stored in confidential files by laboratory document control personnel.

Only data that have met data quality objectives, or data that have acceptable deviations explained, will be submitted by the laboratory. When QA requirements have not been met, the samples will be reanalyzed when possible and only the results of the reanalysis will be submitted, provided they are acceptable.

Data Validation

Data validation (data quality audit) is conducted by the CVRWQCB Project Manager, Petra Lee, to verify whether an analytical method has been performed according to the method and project specifications, and that the results have been correctly calculated and reported. Specific items that are reviewed during data validation are:

- Chain-of-custody records;
- Documentation of the laboratory procedures;
- Accuracy of data reduction, transcription, and reporting;
- Adherence to method-specific calibration procedures and quality control parameters;
- Precision and accuracy of recorded results.

Reconciliation and correction of any uncertain or erroneous data will be initiated by the CVRWQCB Project Manager, Petra Lee. Data will be conveyed to users through the Final Report.

24. RECONCILIATION WITH USER REQUIREMENTS

The diazinon, chlorpyrifos and other organophosphate pesticide concentration data generated in this project will be used by the Regional Board and others for the assessment of pesticides in rainwater that could contribute to contamination of surface waters. Unless it is otherwise qualified, the diazinon and chlorpyrifos data generated in this project will meet the Quality Assurance Objectives listed in Section 14. The reporting limits for diazinon and chlorpyrifos are below recommended criteria for the protection of aquatic ecosystems listed in Section 5.3, so the measurements will be sensitive enough to detect exceedances of these criteria in surface water. The final data report will indicate the level of completeness of the data generated and indicate any times in which data meeting the Quality Assurance Objectives was not obtained.

25. LITERATURE CITED

Bailey, H.C., L. Deanovic, E. Reyes, T. Kimball, K. Larsen, K. Cortwright. V. Connor, and D. Hinton. 2000. *Diazinon and Chlorpyrifos in Urban Waterways in Northern California*. USA. Environmental Toxicology and Chemistry (19) 82-87.

Cusick, W. 2004. *Quality Manual, Revision 2*. California Department of Food and Agriculture, Center for Analytical Chemistry Laboratory. 22.

Majewski, M.S. and D.S. Baston. 2002. *Atmospheric Transport of Pesticides in the Sacramento, California Metropolitan Area, 1996-1997*. U.S. Geological Survey, Water-Resources Investigations Report WRIR-02-4100.

Spector, C, J Karkoski, G Davis. 2004. Concentrations of Pesticides in Sacramento Metropolitan Area Rainwater and Creeks During the 2001, 2002, and 2003 Orchard Dormant Spray Seasons. Central Valley Regional Water Quality Control Board.

USEPA 2004. *Analytical Support Branch Laboratory Operations and Quality Assurance Manual*, November 17, 2004. US Environmental Protection Agency, Science and Ecosystem Support Division, Region 4. Athens, Georgia, USA.

APPENDIX 1. SACRAMENTO URBAN RAIN MONITORING STANDARD OPERATING PROCEDURE (SOP), 2005

Regional Water Quality Control Board
Sacramento Urban Rain Monitoring
Standard Operating Procedure, 2005

Rain Sampling Device

Rainfall samples are collected using a rainfall-sampling device. The device consists of a 19-inch diameter stainless steel bowl with a hole punched in the base, some stainless steel wire, a 3/8-inch diameter stainless steel tube, a 5-gallon bucket and a 2.5-gallon glass carboy. A 3/8-inch diameter piece of stainless steel tubing is placed in the hole of the bowl to guide rainwater into a 2.5-gallon glass carboy set within the bucket. The bowl is secured on top of the 5-gallon plastic bucket with stainless steel wire.

When to Collect Samples

Rain collection will occur for up to five storms during orchard dormant spray season and for up to five storms after orchard dormant spray season. An attempt will be made to deploy the rain collecting devices as close as possible to the beginning of anticipated storm events, generally a day before the forecasted storm event. The targeted accumulated amount of rainfall is a minimum of 0.25 inches in order to collect a sufficient amount of rain. If the rainfall is not collected within 24 hours, the sampling devices will be left until sufficient rainfall for that storm event has occurred. If the storm continues for multiple days with over 0.25 inches of rain, a sample will be collected for each 0.25 inches of rain or every 24 hours (whichever is later) throughout the storm event. Sample collecting equipment will be field cleaned between sample collections when a storm event lasts multiple days.

Equipment Maintenance

Cleaning the Sampling Equipment

Clean all surfaces that will come into contact with the rainwater sample, including the glass carboys, prior to sampling as follows:

1. scrub equipment with warm water and Alconox or Liquinox detergent
2. rinse equipment three times with warm tap water
3. rinse equipment a final time with de-ionized water

Wrap the rainfall-sampling device in a clean plastic bag after washing and rinsing and keep stored in the bag until the sampler is setup at the sampling site.

In some cases mentioned below, a full alconox/liquinox cleaning will not be possible. If this occurs, use the following instructions to do a field rinse of the sampling equipment.

To clean the equipment in the field, pour de-ionized water onto all the surfaces that will come into contact with the sample, including the glass carboy. Rinse the sampling surfaces three times with the de-ionized water, swirling rinsate around in the glass carboy before dumping it onto the ground. Repeat rinsing for a total of three rinses and pour rinsate onto the ground.

When to Clean a Rain-Sampling Device

Clean the rain-sampling device prior to *each* storm and wrap in plastic as stated above. Cleaning the rain-collecting device in the field will be necessary if two days have passed without a storm.

How to Collect Samples

In the field, set up each rain-collecting device in an open area and allow the device to accumulate rain for at least 24 hours. Check the device and if enough rain has been collected, collect sample at that point. If not enough rain has been collected in the first 24 hours, leave device out until enough rain has accumulated for analysis. If the storm event spans over 24 hours and the first sample has already been collected, do a field rinse of the sampler before collecting additional rains samples for that storm event.

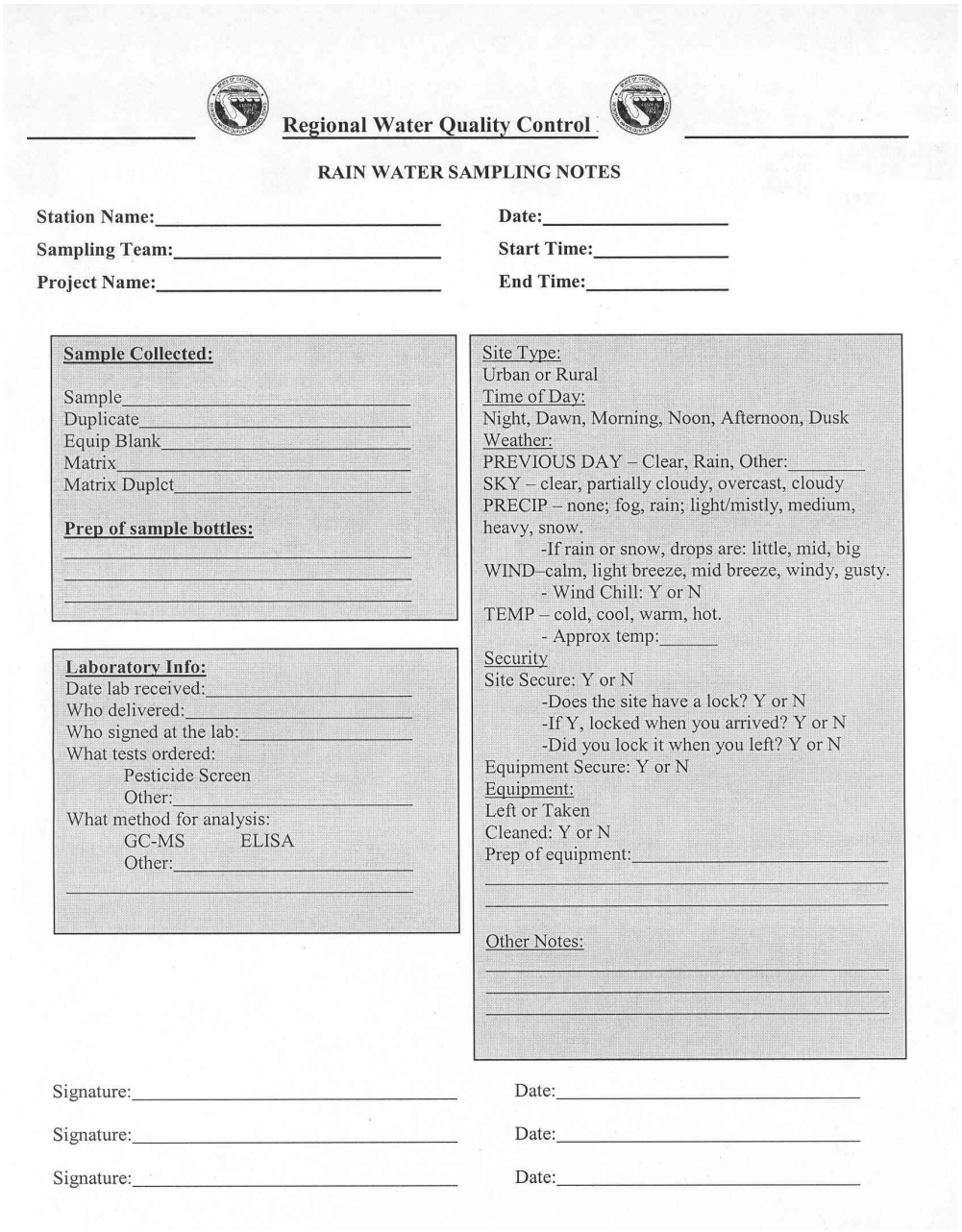
Labeling Bottles

Before collecting the environmental sample(s) or quality assurance/quality control (QA/QC) sample, label the bottle(s) with the pre-prepared labels, including the sample collector's initials and the date. Use the appropriate label based on storm event number (Storm Event 1, Storm Event 2, etc.). Use additional information such as sampler initials, date, rain station (e.g. R3), and whether the sample is a QA/QC sample (e.g. 04 is duplicate sample, 05 is equipment blank, 06 is matrix spike sample, 07 is matrix spike sample duplicate) to determine the sample number. For example, a rain sample collected by George Washington on January 25, 2003 at the R3 site would read GW012503R3; a label for a duplicate of that sample would read GW012503R3-04.

Field Sheets

Complete field sheets at the time the environmental sample, duplicate sample, matrix spike sample, matrix spike sample duplicate, or equipment blank is collected. Complete one field sheet for each site during each of the ten rain-monitoring events that rain samples are collected at. Information on the field sheet will include station name, sampling team, project name, sampling date and time, sample label code(s), site description, location security and conditions, equipment maintenance, and laboratory information. Sign and date the field sheet after filling it out completely and correctly. See Figure 1.

Figure 1 – Regional Board Sample Chain-of Custody



Regional Water Quality Control

RAIN WATER SAMPLING NOTES

Station Name:_____ **Date:**_____

Sampling Team:_____ **Start Time:**_____

Project Name:_____ **End Time:**_____

Sample Collected:

Sample_____
Duplicate_____
Equip Blank_____
Matrix_____
Matrix Duplct_____

Prep of sample bottles:

_____
_____
_____

Laboratory Info:
Date lab received:_____
Who delivered:_____
Who signed at the lab:_____
What tests ordered:
Pesticide Screen
Other:_____
What method for analysis:
GC-MS ELISA
Other:_____
_____

Site Type:
Urban or Rural
Time of Day:
Night, Dawn, Morning, Noon, Afternoon, Dusk
Weather:
PREVIOUS DAY – Clear, Rain, Other:_____
SKY – clear, partially cloudy, overcast, cloudy
PRECIP – none; fog, rain; light/mistly, medium, heavy, snow.
-If rain or snow, drops are: little, mid, big
WIND–calm, light breeze, mid breeze, windy, gusty.
- Wind Chill: Y or N
TEMP – cold, cool, warm, hot.
- Approx temp:_____
Security
Site Secure: Y or N
-Does the site have a lock? Y or N
-If Y, locked when you arrived? Y or N
-Did you lock it when you left? Y or N
Equipment Secure: Y or N
Equipment:
Left or Taken
Cleaned: Y or N
Prep of equipment:_____
_____
_____

Other Notes:
_____
_____
_____

Signature:_____ Date:_____

Signature:_____ Date:_____

Signature:_____ Date:_____

Collecting an Environmental Sample, Environmental Sample Duplicate, Matrix Spike Sample, or Matrix Spike Sample Duplicate

Put on a new clean pair of latex gloves before collecting a new sample or samples. Place one pre-labeled 1-L glass amber bottle per sample onto a stable, flat surface to prevent tipping. Pour a small amount of water from the glass carboy into each 1-L bottle as rinsate. Cap and shake each 1-L bottle and dispose of the rinsate. Repeat this procedure a total of three times and then fill each sample bottle with rainwater and cap the bottle(s) immediately.

In the event that the sampler is left outdoors and more than two days pass before the next storm, clean the rain-sampling device prior to the next forecasted storm. Do a full alconox/liquinox cleaning, but if a full cleaning is not possible, do a field rinse of the device.

Cleaning the collector surfaces just prior to the next storm diminishes the effect that dry deposition could have on sample analysis results.

Collecting Equipment Blanks

Collect equipment blank after the rain-collecting device has had an alconox/liquinox cleaning and/or a field/DI water rinsing. If collecting an equipment blank after the alconox/liquinox cleaning, deploy the device and then collect an equipment blank immediately afterwards (before rain has contaminated the surface). Pour de-ionized water over all contact surfaces of the set-up rain-sampling device (inside surfaces of the stainless steel bowl and pipe) and into the glass carboy. You will need to pour enough de-ionized water into the device to fill a 1-L amber glass bottle. Pour a minimum of 1-L of de-ionized water over all the surfaces of the rain-collecting device that will come into contact with the rainwater. Once water has collected in the carboy, rinse bottle three times with rinsate, then pour the water into the 1-L amber glass bottle and label the bottle appropriately.

If collecting an equipment blank after doing a field/DI water rinse, rinse all surfaces that will come into contact with the rain three times with DI water as indicated above in the cleaning section. After rinsing the device three times and dumping the rinsate, pour at least 1-L of DI water over all surfaces that will come into contact with the rain. Rinse the sample bottle three times with the rinsate and then pour 1-L of rinsate into the 1-L amber glass bottle and label the bottle appropriately.

Sample Transport and Custody

Storing the Sample

Store the sample(s) in foam sleeves on ice while in the field and in 4ºC refrigerator or in an ice-chest filled with ice until the sample(s) are transported to the lab. Transfer sample(s) to the lab on the same day of sampling or on the next business day. Store samples in a secure area until delivery if immediate transport to the lab is not possible.

Chain-of-Custody (COC)

Complete the chain-of-custody and fill out all entries on the chain-of-custody form for all chemical analyses before transferring the sample(s) to the lab.

Samples need to be in Regional Board staff's possession so that Regional Board staff can deliver samples to:

California Department of Food and Agriculture

Center for Analytical Chemistry (CDFA Lab)
3292 Meadowview Road
Sacramento, CA 95832

To relinquish the samples to CDFA staff, sign and date the COC along with CDFA staff, and release the original completed COC to CDFA staff. Obtain a copy of the completed COC with both signatures for Regional Board records before leaving the CDFA Lab. See figure 2 for an example of a Regional Board chain-of-custody.

Figure 2 – Sample Regional Board Chain-of-Custody

STATE OF CALIFORNIA — ENVIRONMENTAL PROTECTION AGENCY
REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION
11020 SUN CENTER DRIVE #200 ? RANCHO CORDOVA, CA 95670-6114
PHONE: (916) 464-3291 ? FAX (916) 464-4645

CHAIN OF CUSTODY

PROGRAM	PCA	PROJECT NAME
SAMPLER (Signature)	PRINT NAME	

SAMPLE				CONTAINER		MATRIX			COMPOSITE	GRAB	PRESERVATIVES	ANALYSIS REQUIRED									FIELD CONDITIONS (TEMP, WIND, ETC.)
IDENTIFICATION	LOCATION	DATE	TIME	TYPE	NO.	WATER	WASTE-WATER	SOIL / SLUDGE													LAB NO.

SPECIAL INSTRUCTIONS / SUSPECTED CONSTITUENTS

RELINQUISHED BY (Signature)	DATE / TIME	RECEIVED BY (Signature)	RELINQUISHED BY (Signature)	DATE / TIME	RECEIVED BY (Signature)

APPENDIX 2. MULTI-RESIDUE METHOD FOR EXTRACTION AND ANALYSIS OF PESTICIDES IN SURFACE WATER

Multi-Residue Method for Extraction and Analysis
of Pesticides in Surface Water

1. Scope: To provide a standard procedure for the extraction and analysis of a broad range of pesticides in surface water using a Mass selective detector (MSD).

2. Outline:

- Apparatus
- Reagents and Supplies
- Method of Sample Preparation
- Methods of Analysis

3. References:

Methods of Analysis by the US Geological Survey National Water Quality Laboratory- Determination of Pesticides in Water by C18 SPE and capillary-Column GC/MS with SIM. By Steven D. Zaugg. et el

U.S. Environmental Protection Agency. 1971. Method for Organic Pesticides in Water and Wastewater. National Environmental Research Center. Cincinnati. Ohio

STANDARD METHODS For The EXAMINATION OF WATER AND WASTEWATER. 18th EDITION 1992. 6630 ORGANOCHLORINE PESTICIDES 6-101

4. Specific Procedures:

4.1 Apparatus

- 2-liter size Separatory Funnels
- 250 mL roundbottom flasks
- Glass Filter Funnel with glass wool and Na2SO4
- Rotavapor evaporator
- Nitrogen evaporator
- VWR vrtex genie or equivalent
- 15 mL collection tubes
- Agilent Model 5973 GC-MSD operated in SIM mode
- Vacuum apparatus with funnels and collection containers

4.2 Reagents and Supplies

- Methylene chloride, nanograde or equivalent pesticide grade
- Glass wool
- NaCl: Certified A.C.S. (Fisher Chemical)
- 0.45µ nylon filters (Alltech 2024 or equivalent)
- Sodium sulfate/methylene chloride rinsed and dried

4.3 Method of Sample Preparation:

4.3.1 For MSD analysis:

a) Weigh and record the 1-liter size water sample.
b) Spike using 500µL surrogate spiking solution: 0.25µg/mL Chlorpyrifos methyl.

c) For the spike sample: spike 500µL appropriate spike solution.
d) Empty approximately 500mL of the sample into a 2-liter size separatory funnel. Weigh and record the sample bottle. Add in approx 10-15g of granular sodium chloride. Shake gently to dissolve salt.
e) Add in 60ml of methylene chloride. Shake well for three minutes. Let settle until the lower methylene chloride layer is completely separated from the above water layer. Filter bottom organic layer through a bed of granular anhydrous sodium sulfate (approx. 20g) into 250ml round bottom flask.
f) Repeat step e above two more times. Place round bottom flask on Rotavapor evaporator and evaporate to 5-7 mL's at 40° C. Transfer contents of round bottom flask to a 15mL collection tube. Rinse round bottom flask with 5ml methylene chloride and add to collection tube. Place 15mL collection tube on N-Evaporator with water temperature set at 40°C. Evaporate the sample to just dryness. Remove sample from N-Evaporator and carefully add 0.5ml of methylene chloride and 5.0µL of 5.0µg/mL internal standard solution into test tube with sample. Vortex and transfer into autosampler vial. Cap and store vials in -5^{0}C freezer until ready for analysis.

4.4 Method of analysis:

4.4.1 For GC-MSD: Agilent Model 5973 GC-MSD

a) GC Parameters:
GC Column: HP-5MS or equivalent; 30meter; 0.25mm x 0.25um film thickness.
Injector temperature initial at 230C
Injection Volume = 2ul

b) GC-MSD Parameters:
Selective Ion Monitoring Mode
EM Voltage: Abs 3000Volt (Max)
Tune & Tune file: Max. Sensitivity Auto Tune

c) Pesticides Monitored:

	LOD* (ppb)	LOQ** (ppb)
Eptam (EPTC)	0.020	0.05
Simazine	0.005	0.20
Diazinon	0.007	0.02
Carbaryl	0.007	0.02
Metalochlor	0.007	0.02
Chlorpyrifos	0.004	0.01
Cyanazine	0.007	0.05
Dacthal (DCPA)	0.007	0.05
Methidathion	0.010	0.03
Propargite	0.15	0.50
Azinphos methyl	0.007	0.05

*LOD - Limit of Detection
**LOQ – Limit of Quantification

Surrogate: Chlorpyrifos methyl - 250ppt
Internal standard: Anthracene-d10, Pyrene-d10, & Chrysene-d12 (500ppt)

d)Selective Ion Monitoring Parameters:
The Segment Start Time and SIM ions needed to be updated by the operation chemist from time to time due to instrument conditions or whenever new compounds are added or deleted. Maximum SIM Ions allowed per segment time is 30.

Total SIM Segments: 6

Group 1	Start Time:	4.00				
	SIM Ions:	86	128	164	173	(7)
		186	189	201		
Group 2	Start Time:	15.50				
	SIM Ions:	88	115	125	137	(13)
		144	179	186	188	
		201	274	286	288	
		304				
Group 3	Start Time:	19.50				
	SIM Ions:	162	197	198	204	(10)
		238	240	258	301	
		314	332			
Group 4	Start Time:	23.00				
	SIM Ions:	85	125	145		(3)
Group 5	Start Time:	26.00				
	SIM Ions:	77	132	135	141	(12)
		160	165	166	173	
		181	209	240	350	
Group 6	Start Time:	32.00				
	SIM Ions:	163	165	167	181	
		225	226	419		

TEMPERATURE:

Injector Temperature. 230ºC

Oven Temperature Programming:

Initial temperature 70ºC hold for 2.00 min.

Level	Rate (ºC/min)	Final Temperature (ºC)	Final Time
1	25	150	0.0
2	3	200	0.0
3	8	280	12.0

a) Method calibration
Five levels of standards are prepared in matrix of reagent grade water to calibrate the analysis method. A linear regression is used including 0,0. The R squared value should be greater or equal to 0.99. Standards are run with the sample set to check for calibration integrity. Continuing calibration standard values should be within ±25% of

calibration. Residue concentration is taken from instrument report table and calculated. If the residue amount falls outside the calibration curve, the sample will be diluted and reanalyzed.

$$\text{Residue Amt (ppt)} = \frac{(\text{Instrument amt} \times 500\text{g})}{\text{Weight of sample}}$$

If R squared value of calibration curve is <0.99, the pesticide level may be determined by direct comparison of residue response to the average response of the nearest bracketing standard concentration. Response of bracketing standards should not vary more than 25%. The residue response should fall within ±30% of standard response. If the residue amount falls outside calibration curve, the sample will be diluted and reanalyzed. A non-linear calibration may be necessary to achieve low detection limits or address specific instrumental techniques. Non-linear calibration is not to be used to compensate for detector saturation or to avoid instrument maintenance.

Calculation using single point comparisons:

$$\text{Sample amt (ppt)} = \left(\frac{\text{Sample response}}{\text{Avg response of bracketing stds}}\right) \times \left(\frac{500\text{g}}{\text{Weight of sample (g)}}\right) \times \text{Std amt}$$

4.5 Method Verification

Level 1 Day 1

Compound	Std. Conc.	Std before ppb	Std after Ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	50	63.07	62.87	0.3	62.97	26.96	42.8
Simazine	200	163.39	154.22	5.8	158.805	128.63	81.0
Diazinon	20	21.89	20.37	7.2	21.13	16.31	77.2
Chlorpyrifos methyl	50	43.68	40.86	6.7	42.27	32.94	77.9
Carbaryl	20	18.4	17.56	4.7	17.98	15.45	85.9
Metolachlor	20	22.44	21.23	5.5	21.835	18.02	82.5
Chlorpyrifos	10	6.84	6.19	10.0	6.515	5.65	86.7
Cyanazine	50	46.63	42.77	8.6	44.7	38.03	85.1
Dacthal (DCPA)	50	55.55	54.2	2.5	54.875	43.85	79.9
Methidathion	30	24.5	21.44	13.3	22.97	19.61	85.4
Propargite	500	395.81	365.33	8.0	380.57	304.01	79.9
Azinphos methyl	50	38.57	39.49	-2.4	39.03	31.06	79.6

Level 3 Day 1

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	200	207.87	204.84	1.5	206.355	91.8	44.5
Simazine	800	764.11	741.1	3.1	752.605	596.71	79.3
Diazinon	100	117.91	109.53	7.4	113.72	83.7	73.6
Chlorpyrifos methyl	200	181.72	171.92	5.5	176.82	130.78	74.0
Carbaryl	100	110.86	109.51	1.2	110.185	84	76.2
Metolachlor	100	130.04	124.47	4.4	127.255	104.38	82.0
Chlorpyrifos	50	35.22	34.16	3.1	34.69	27.46	79.2
Cyanazine	200	160.66	154	4.2	157.33	127.43	81.0
Dacthal (DCPA)	200	188.63	188.16	0.2	188.395	146.59	77.8
Methidathion	100	96.13	88	8.8	92.065	75.08	81.6
Propargite	1000	894.36	876.05	2.1	885.205	752.51	85.0
Azinphos methyl	200	153.05	144.27	5.9	148.66	123.84	83.3

Level 5 Day 1

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	1000	949.89	954.86	-0.5	952.375	433.73	45.5
Simazine	1200	1277.66	1206.8	5.7	1242.23	986.37	79.4
Diazinon	1000	976.27	923.75	5.5	950.01	712.86	75.0
Chlorpyrifos methyl	1000	938.06	906.41	3.4	922.235	667.62	72.4
Carbaryl	1000	989.33	747.69	27.8	868.51	750.72	86.4
Metolachlor	1000	934.85	886.54	5.3	910.695	717.68	78.8
Chlorpyrifos	500	502.41	477.94	5.0	490.175	375.71	76.6
Cyanazine	1000	998.22	1003.03	-0.5	1000.625	783.29	78.3
Dacthal (DCPA)	1000	965.57	976.13	-1.1	970.85	731.6	75.4
Methidathion	1000	976.54	873.36	11.2	924.95	733.07	79.3
Propargite	2000	2200.46	2213.68	-0.6	2207.07	1624.18	73.6
Azinphos methyl	1000	990.91	849.49	15.4	920.2	674.09	73.3

Level 1 Day 2

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% Recovery
EPTC (Eptam)	50	62.87	63.6	-1.2	63.24	54.34	85.9
Simazine	200	154.22	162.91	-5.5	158.57	155.38	98.0
Diazinon	20	20.37	21.54	-5.6	20.96	21.97	104.8
Chlorpyrifos methyl	50	40.86	43	-5.1	41.93	41.23	98.3
Carbaryl	20	17.56	19.45	-10.2	18.51	19.35	104.6

Metolachlor	20	21.23	21.6	-1.7	21.42	21.07	98.4
Chlorpyrifos	10	6.19	6.2	-0.2	6.20	6.64	107.2
Cyanazine	50	42.77	46.75	-8.9	44.76	46.27	103.4
Dacthal (DCPA)	50	54.2	55.1	-1.6	54.65	53.91	98.6
Methidathion	30	21.44	23.14	-7.6	22.29	24.07	108.0
Propargite	500	365.33	416.06	-13.0	390.70	410.92	105.2
Azinphos methyl	50	39.49	41.11	-4.0	40.30	47.88	118.8

Level 3 Day 2

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% Recovery
EPTC (Eptam)	200	204.84	207.68	-1.4	206.26	127.47	61.8
Simazine	800	741.1	750.43	-1.3	745.765	712.57	95.5
Diazinon	100	109.53	111.3	-1.6	110.415	106.99	96.9
Chlorpyrifos methyl	200	171.92	175.16	-1.9	173.54	161.52	93.1
Carbaryl	100	109.51	102.83	6.3	106.17	96.76	91.1
Metolachlor	100	124.47	124.56	-0.1	124.515	123.21	99.0
Chlorpyrifos	50	34.16	36.5	-6.6	35.33	33.99	96.2
Cyanazine	200	154	154.18	-0.1	154.09	156.29	101.4
Dacthal (DCPA)	200	188.16	186.78	0.7	187.47	180.96	96.5
Methidathion	100	88	86.66	1.5	87.33	84.67	97.0
Propargite	1000	876.05	850.46	3.0	863.255	822.54	95.3
Azinphos methyl	200	144.27	139.33	3.5	141.8	148.53	104.7

Level 5 Day 2

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% Recovery
EPTC (Eptam)	1000	954.86	949.22	0.6	952.04	690.4	72.5
Simazine	1200	1206.8	1222.11	-1.3	1214.455	1209.03	99.6
Diazinon	1000	923.75	961.76	-4.0	942.755	898.6	95.3
Chlorpyrifos methyl	1000	906.41	913.68	-0.8	910.045	858.32	94.3
Carbaryl	1000	947.69	875.18	8.0	911.435	879.64	96.5
Metolachlor	1000	886.54	892.46	-0.7	889.5	878.99	98.8
Chlorpyrifos	500	477.76	484.31	-1.4	481.035	473.38	98.4
Cyanazine	1000	1003.03	957.69	4.6	980.36	985.87	100.6
Dacthal (DCPA)	1000	976.13	953.99	2.3	965.06	925.06	95.9
Methidathion	1000	873.36	841.7	3.7	857.53	884.36	103.1
Propargite	2000	2213.68	1960.49	12.1	2087.085	2131.15	102.1
Azinphos methyl	1000	849.49	807.21	5.1	828.35	997.29	120.4

Level 1 Day 3

	Std.	Std before	Std after	%	Average	Sample	%

Compound	Conc.	ppb	ppb	Diff.	ppb	ppb	recovery
EPTC (Eptam)	50	71.05	71.59	-0.8	71.32	57.03	80.0
Simazine	200	161.99	172.25	-6.1	167.12	141.4	84.6
Diazinon	20	22.11	23.07	-4.2	22.59	21.34	94.5
Chlorpyrifos methyl	50	49.55	51.55	-4.0	50.55	42.85	84.8
Carbaryl	20	23.86	27.11	-12.8	25.485	19.82	77.8
Metolachlor	20	25.49	27.7	-8.3	26.595	23.18	87.2
Chlorpyrifos	10	6.6	6.43	2.6	6.515	5.69	87.3
Cyanazine	50	48.41	54.71	-12.2	51.56	44.3	85.9
Dacthal (DCPA)	50	62.47	63.86	-2.2	63.165	55.8	88.3
Methidathion	30	30.97	34.02	-9.4	32.495	25.09	77.2
Propargite	500	492.2	524.97	-6.4	508.585	333.79	65.6
Azinphos methyl	50	61.64	66.16	-7.1	63.9	48.07	75.2

Level 3 Day 3

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample Ppb	% recovery
EPTC (Eptam)	200	241.51	245.78	-1.8	243.645	89.36	36.7
Simazine	800	861.72	822.15	4.7	841.935	581.61	69.1
Diazinon	100	142.65	137.29	3.8	139.97	96.19	68.7
Chlorpyrifos methyl	200	228.46	220.89	3.4	224.675	149.7	66.6
Carbaryl	100	160.2	142.63	11.6	151.415	112.14	74.1
Metolachlor	100	170.09	165.99	2.4	168.04	126.69	75.4
Chlorpyrifos	50	41.58	37.04	11.5	39.31	26.56	67.6
Cyanazine	200	201.99	186.77	7.8	194.38	143.89	74.0
Dacthal (DCPA)	200	230.1	228.09	0.9	229.095	174.03	76.0
Methidathion	100	139.22	126.9	9.3	133.06	99.62	74.9
Propargite	1000	1172.44	1044.98	11.5	1108.71	828.31	74.7
Azinphos methyl	200	241.31	210.59	13.6	225.95	340.4	150.7

Level 5 Day 3

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	1000	1115.44	1106.25	0.8	1110.845	757.42	68.2
Simazine	1200	1296.962	1408.62	-8.3	1352.791	1077.03	79.6
Diazinon	1000	1173.82	1221.56	-4.0	1197.69	946.29	79.0
Chlorpyrifos methyl	1000	1129.67	1193.45	-5.5	1161.56	882.91	76.0
Carbaryl	1000	1162.97	1414.12	-19.5	1288.545	1048.09	81.3
Metolachlor	1000	1156.79	1235.73	-6.6	1196.26	959.17	80.2
Chlorpyrifos	500	513.18	554.31	-7.7	533.745	423.76	79.4
Cyanazine	1000	1148.15	1218.92	-6.0	1183.535	980.75	82.9
Dacthal (DCPA)	1000	1123.9	1148	-2.1	1135.95	937.57	82.5

Methidathion	1000	1176.09	1448.52	-20.8	1312.305	976.82	74.4
Propargite	2000	2180.32	2496.83	-13.5	2338.575	1865.54	79.8
Azinphos methyl	1000	1118.15	1423.93	-24.1	1271.04	937.16	73.7

Level 1
All compounds at our LOQ

Compound	Std. Conc.(ppt)	Day 1	Day 2	Day 3	Average Recovery	% RSD	SD
EPTC (Eptam)	50	42.8	85.9	80.0	69.6	46.7	23.4
Simazine	200	81.0	98.0	84.6	87.9	4.5	9.0
Diazinon	20	77.2	104.8	94.5	92.2	69.7	13.9
Chlorpyrifos methyl	50	77.9	98.3	84.8	87.0	20.8	10.4
Carbaryl	20	85.9	104.6	77.8	89.4	68.7	13.7
Metolachlor	20	82.5	98.4	87.2	89.4	40.8	8.2
Chlorpyrifos	10	86.7	107.2	87.3	93.7	116.7	11.7
Cyanazine	50	85.1	103.4	85.9	91.5	20.7	10.3
Dacthal (DCPA)	50	79.9	98.6	88.3	88.9	18.7	9.4
Methidathion	30	85.4	108.0	77.2	90.2	53.2	16.0
Propargite	500	79.9	105.2	65.6	83.6	4.0	20.1
Azinphos methyl	50	79.6	118.8	75.2	91.2	48.0	24.0

Level 3
All compounds at approx 4 times LOQ

Compound	Std. Conc.(ppt)	Day 1	Day 2	Day 3	Average Recovery	% RSD	SD
EPTC (Eptam)	200	44.5	61.8	36.7	47.7	6.4	12.8
Simazine	800	79.3	95.5	69.1	81.3	1.7	13.3
Diazinon	100	73.6	96.9	68.7	79.7	15.1	15.1
Chlorpyrifos methyl	200	74.0	93.1	66.6	77.9	6.8	13.7
Carbaryl	100	76.2	91.1	74.1	80.5	9.3	9.3
Metolachlor	100	82.0	99.0	75.4	85.5	12.2	12.2
Chlorpyrifos	50	79.2	96.2	67.6	81.0	28.8	14.4
Cyanazine	200	81.0	101.4	74.0	85.5	7.1	14.2
Dacthal (DCPA)	200	77.8	96.5	76.0	83.4	5.7	11.4
Methidathion	100	81.6	97.0	74.9	84.5	11.3	11.3
Propargite	1000	85.0	95.3	74.7	85.0	1.0	10.3
Azinphos methyl	200	83.3	104.7	150.7	112.9	17.2	34.4

Level 5
All compounds at aprox 20 times LOQ

Compound	Std. Conc.(ppt)	Day 1	Day 2	Day 3	Average Recovery	% RSD	SD
EPTC (Eptam)	1000	45.5	72.5	68.2	62.1	1.5	14.5
Simazine	1200	79.4	99.6	79.6	86.2	1.0	11.6

Diazinon	1000	75.0	95.3	79.0	83.1	1.1	10.8
Chlorpyrifos methyl	1000	72.4	94.3	76.0	80.9	1.2	11.7
Carbaryl	1000	86.4	96.5	81.3	88.1	0.8	7.7
Metolachlor	1000	78.8	98.8	80.2	85.9	1.1	11.2
Chlorpyrifos	500	76.6	98.4	79.4	84.8	2.4	11.9
Cyanazine	1000	78.3	100.6	82.9	87.3	1.2	11.8
Dacthal (DCPA)	1000	75.4	95.9	82.5	84.6	1.0	10.4
Methidathion	1000	79.3	103.1	74.4	85.6	1.5	15.4
Propargite	2000	73.6	102.1	79.8	85.2	0.7	15.0
Azinphos methyl	1000	73.3	120.4	73.7	89.1	2.7	27.1

Single day variation Day 1

Compound	Level 1	Level 3	Level 5	Average	Std. Dev.
EPTC (Eptam)	42.8	44.5	45.5	44.3	1.4
Simazine	81.0	79.3	79.4	79.9	1.0
Diazinon	77.2	73.6	75.0	75.3	1.8
Chlorpyrifos methyl	77.9	74.0	72.4	74.8	2.8
Carbaryl	85.9	76.2	86.4	82.8	5.8
Metolachlor	82.5	82.0	78.8	81.1	2.0
Chlorpyrifos	86.7	79.2	76.6	80.8	5.2
Cyanazine	85.1	81.0	78.3	81.5	3.4
Dacthal (DCPA)	79.9	77.8	75.4	77.7	2.3
Methidathion	85.4	81.6	79.3	82.1	3.1
Propargite	79.9	85.0	73.6	79.5	5.7
Azinphos methyl	79.6	83.3	73.3	78.7	5.1

Single day variation Day 2

Compound	Level 1	Level 3	Level 5	Average	Std. Dev.
EPTC (Eptam)	85.9	61.8	72.5	73.4	12.1
Simazine	98.0	95.5	99.6	97.7	2.1
Diazinon	104.8	96.9	95.3	99.0	5.1
Chlorpyrifos methyl	98.3	93.1	94.3	95.2	2.7
Carbaryl	104.6	91.1	96.5	97.4	6.8
Metolachlor	98.4	99.0	98.8	98.7	0.3
Chlorpyrifos	107.2	96.2	98.4	100.6	5.8
Cyanazine	103.4	101.4	100.6	101.8	1.4
Dacthal (DCPA)	98.6	96.5	95.9	97.0	1.4
Methidathion	108.0	97.0	103.1	102.7	5.5
Propargite	105.2	95.3	102.1	100.9	5.1
Azinphos methyl	118.8	104.7	120.4	114.6	8.6

Single day variation Day 3

Compound	Level 1	Level 3	Level 5	Average	Std. Dev.	
EPTC (Eptam)	80.0	36.7	68.2	61.6	22.4	
Simazine	84.6	69.1	79.6	77.8	7.9	
Diazinon	94.5	68.7	79.0	80.7	13.0	
Chlorpyrifos methyl	84.8	66.6	76.0	75.8	9.1	
Carbaryl	77.8	74.1	81.3	77.7	3.6	
Metolachlor	87.2	75.4	80.2	80.9	5.9	
Chlorpyrifos	87.3	67.6	79.4	78.1	9.9	
Cyanazine	85.9	74.0	82.9	80.9	6.2	
Dacthal (DCPA)	88.3	76.0	82.5	82.3	6.2	
Methidathion	77.2	74.9	74.4	75.5	1.5	
Propargite	65.6	74.7	79.8	73.4	7.2	
Azinphos methyl	75.2	150.7	73.7	99.9	44.0	*

Revision Log:

Date	What was Revised? Why?
1/23/05	**Changed surrogate concentration to 250 ppt.**
1/26/05	**Added in Department SOP headers.**
2/7/2005	**Removed synthetic pyrethroid compounds.**

Approvals:

Written By:

_____ _____
Stephen Siegel Date
Agricultural Chemist III (Supervisor)

Approved By:

_____ _____
S. Mark Lee, Ph.D. Date
Research Agricultural Chemist

Approved By:

_____ _____
Harnek Nijjar Date
Quality Assurance Officer

APPENDIX 3. ROUTINE OPERATION AND MAINTENANCE OF BUCHI ROTARY EVAPORATOR

Routine Operation and Maintenance of Rotary Evaporator

1. Purpose:

This procedure is to be used for the basic operation, routine maintenance and troubleshooting of the rotary evaporator.

2. Scope:

This procedure applies to the rotary evaporator and shall be followed by all authorized personnel in the Center.

3. Definitions Not in Glossary:

Cold finger: a round-bottomed, open top, double walled container, with a lower and upper vent for in-line vacuum condensation. The open top permits easy filling of the container with wet ice or dry ice and liquid to cool vapors rising between the walls and condense them into a receiving flask. This is a backup condensation device to prevent vaporized solvent from contaminating the vacuum pump.

DI-water: deionized or distilled water

4. Outline of Procedures:

- General Evaporation Considerations
- Description of Components and Operation of the Rotary Evaporator System
- Safety
- System Maintenance and Troubleshooting

5. Specific Procedures:

5.1 General Evaporation Considerations

5.1.1 Determine solvent's boiling point and set the water bath 10-20 °C below this point. The analytical method may specify a water bath temperature other than the range listed above. If necessary, adjust temperature of the water bath and allow it to equilibrate. If water temperature is higher than desired, add ice to cool bath to desired temperature. If water temperature is lower, adjust heater higher and allow to equilibrate.

5.1.2 Use DI-water exclusively in the water bath. Fill to approximately 2 cm (¾") from top of bath as a general rule when evaporating solvent from 500 mL boiling flasks.

5.1.3 Clean all sample to apparatus contacts with solvent before starting to rotary evaporate a sample.

5.1.4 Empty both condenser and cold finger collection flasks before evaporating a set of samples.

5.1.5 Check all coolant and vacuum connections for leaks or wear before starting rotary evaporation system.

5.2 Description of Components and Operation of the Rotary Evaporator System

5.2.1 The basic components consist of the following: a water bath, a vacuum pump, a cold finger and collecting flask, a chiller with a recirculating pump, a condensing column with a rotary steam vent and collecting flask for condensed solvent. A cold finger is optional.

5.2.2 Turn on chiller and allow to circulate for at least 10 minutes. Check temperature reading on front of chiller or feel tubing near condenser to make sure that the flow is cold.

5.2.3 Turn on water bath and adjust to desired temperature. Adjust water level with DI-water according to flask size.

5.2.4 Add ice to cold finger. Some sections use wet ice. If using dry ice, follow precautions listed in the Safety section 5.3.3.

5.2.5 Solvent clean the steam vent glass fitting before and after evaporating a sample. Collect the solvent washings in a waste beaker and empty into the correct waste solvent container in the hood.

5.2.6 When water bath has reached temperature attach flask to unit and clamp securely.

5.2.7 Turn on vacuum pump and adjust vacuum according to the solvent you are evaporating or the method specifications. Most solvents will evaporate well at a vacuum of 15 inches of mercury (Hg).

5.2.8 In-line vacuum selectors determine which flask/s are under a vacuum. Flow lines on the thumb holds show the direction of vacuum flow.

5.2.9 Turn rotating speed dial to begin flask rotation. If flask is quite full, begin very slowly and increase speed as solvent evaporates. If necessary, adjust water bath temperature or vacuum to control evaporation rate.

5.2.10 Lower flask into the water gradually to approximately the level of solvent in the flask. If the solvent is less than 100 mL or if it begins to boil, adjust flask height so that a rapid solvent loss is avoided.

5.2.11 Refer to the analytical method to verify the target sample volume. If specified in the method, add an exchange solvent/s and continue to evaporate until all the extraction solvent is evaporated and the approximate volume is achieved.

5.2.12 Raise flask from water bath and switch off the rotator. Vent vacuum slowly and remove flask from unit and proceed to the next step specified in the analytical method. The combi-clip may be used to remove a frozen flask from the steam vent (turn clock-wise) or to remove a jammed steam vent by moving it in the opposite directions on the threaded steam vent (Büchi pre-series R-200).

5.2.11 Depending on need, either turn off water bath and coolant pump or leave them on for the next analyst. Be sure to turn off bath and pump at the end of the day.

5.3 Safety

5.3.1 Before operation, check that all plugs and cords are in good working order and that they are plugged into the correct outlets and that they are not over loaded.

5.3.2 Check all coolant connections for leaks.

5.3.3 Use gloves to handle dry ice. Never touch dry ice with bare skin (-79 ˚C). Slowly and carefully add dry ice to cold finger.

5.3.4 Check all vacuum hose connections for a tight fit. Check for any cracking or leaks in the lines.

5.3.5 Check that the cooler-recirculator has at least 8 inches of open space around unit.

5.3.6 Check that the boiling flask has no cracks. The flask possibly implodes when vacuum pressure is applied. Quantitatively transfer to a good flask with rinses, if any cracks are found.

5.4 System Maintenance and Troubleshooting

5.4.1 Check the following monthly:

5.4.1.1 Ethylene glycol level in cold finger is ~ 1/2 full

5.4.1.2 Air intakes of chiller and vacuum pump are clean and free of any obstruction

5.4.1.3 Coolant level in chiller is at the proper level

5.4.1.4 All glass joints are easy to separate and are not frozen

5.4.1.5 Water bath has no debris or sediment in it

5.4.2 Check the following yearly:

5.4.2.1 Air intakes of chiller and vacuum pump are clean and free of any obstruction

5.4.2.2 Cooling coils of the chiller are clean and free of any obstruction; if not, use a vacuum cleaner with the brush attachment to clean

5.4.2.3 Check coolant density and level. Add or change as needed

6. References:

None

7. Comments:

None

Reviewed By:

_____ _____

Terry Jackson Date
Quality Assurance Officer

Approved By:

_____ _____
William Cusick Date
Branch Chief

Revision Log:

Date	Revision #	Reason for Revision	Approved By	Date

APPENDIX 4. ROUTINE OPERATION AND MAINTENANCE OF AGILENT /HP GC-MSD

CDFA/CAC Control Document
Uncontrolled copy
1/27/2005 Stephen Siegel

Routine Operation and Maintenance of Agilent /HP GC-MSD

1. Purpose:

This procedure is to be used for the start-up, shut-down, routine maintenance, and troubleshooting of Agilent (HP) GC-MSD (5971/5972/5973).

2. Scope:

This procedure applies to GC/MSD and shall be followed by all authorized personnel in the Center.

3. Definitions not in Glossary:

Detector Temperature: This term is used to refer to the transfer – line interface temperature.
EI: Electron Ionization.
EM: Electron Multiplier.
EV: Electron Volt.

4. Outline of Procedures:

- Instrument Start-up
- Instrument Shut-down
- Instrument Maintenance
- Instrument Troubleshooting

5. Specific Procedures:

5.1 Instrument Start-up

See Agilent Technologies 5973 Network Hardware Manual Chapter 2 Operating the MSD p 34
5972A MSD Manual Chapter 2, p 35
5971A MSD Manual Chapter 4, p 4 -1

5.1.1 Make sure that the computer is turned on. Turn on the GC, and make sure that all the temperatures are OFF. It is OK to allow 5-10 psi of helium to flow through the system.
5.1.2 Make sure that MSD source and its connecting cables are in perfect order and the main compartment's gasket seal is in place and the vent-valve (5973 model) is closed. For the 5971 and 5972 MSD, make sure that the transfer-line interface unit is secured in place.
5.1.3 Make sure that a GC column has been connected to the MSD.
5.1.4 With one hand firmly holdon to the MSD unit; switch the main power to the MSD on. Release holding as soon as the vacuum seals the MSD unit in place.
5.1.5 Open up "Instrument Top" view and go to "Instrument control"
5.1.6 From the "Diagnostic and vacuum control" view, select "Pump Down".
5.1.7 Let the system pump down for 20-30 minutes before turning the oven temperature, detector temperature and injector temperature back on.
5.1.8 For the 5973 MSD, reset the MS temperatures if it has not already done so.
5.1.9 Set the oven temperature between 160-200 ° C for approximately 3-4 hr before using the MSD.
5.1.10 Instrument Pre-run system check
Mass spectrometer vacuum:

Under normal operation condition, the Ion gauge reading of the vacuum shall be 2.0 X 10^{-5} Torr or lower with the fore-pump pressure between 30-50 Torr.(See Agilent Technologies 5973 Network MSD
Hardware Manual pp. 46-47.5972A Manual, also at pp. 46-47.

5.1.10.1 Mass spectrometer air and water check

5.1.10.1.1 Set the GC oven temperature between 120-160 °C.
5.1.10.1.2 From the "Instrument Control", go to "Diagnostics and vacuum control" view and select "Air and Water Check".
5.1.10.1.3 The abundance of ions at m/z 18 (water) and m/z 28 (nitrogen) shall be less than10% of the abundance of 69($CF3^+$, 100%, base peak fragment ions of the tuning compound, PFTBA). Or according to the of the specification method's SOP.
5.1.10.1.4 A print out report shall be used as a record.

5.1.11 Mass Spectrometer Tune and Calibration:
5973 Manual Chapter 2, p 50
5972 Manual Chapter 2, p 56
5971 Manual Chapter 4, p 4-35

5.1.11.1 Tune Compound: Perfluoro-tri-n-butyl amine [PFTBA, $(C_4F_9)_3N$],
5.1.11.2 Set the GC oven temperature at the temperature range where the expected analytes elute. In general set the GC oven temperature 20-150 °C. or follow the specification of the method.
5.1.11.3 Instrument Auto tune:
5.1.11.4 Go to the "Instrument Control" View
5.1.11.5 Go to Perform MS "Auto Tune" or "Manual Tune".
5.1.11.6 Select one of the following tune options Autotune
Standard Spectra Autotune
DFTPP Tune
Maximum Sensitivity Autotune
5.1.11.7 Save the tune file and keep the print-out of the tune file for a record.

5.2 Instrument Shut-down
It is not necessary to completely shut-down the MSD after data acquisition. The system may be left in stand-by mode.

5.2.1 Instrument stand-by mode:

5.2.1.1 In general, set the GC temperature between 80-100 °C
5.2.1.2 Set GC Injector temperature between 200-230°C.
5.2.1.3 Set detector temperature at 280 °C.
5.2.1.4 Set the helium head pressure between 5-8 psi.

5.2.2 System complete shut-down
A complete shut-down of the GC-MSD is necessary for MSD service and maintenance. Also some GC service requires shut-down.

5.2.2.1 If the system is equipped with an ion gauge controller, switch off the ion gauge.
5.2.2.2 Go to the "Instrument Control" and go to "Diagnostics and Vacuum Control". Select Vent. Follow the instructions. (See also Agilent Technologies 5973 Network Hardware Manual pp. 54-56)

5.2.2.3 Shut off the oven temperature, detector temperature, and GC Injector inlet temperature.
5.2.2.4 Wait for the vent cycle to complete (approx 30-40 min.).
5.2.2.5 For the 5973 MSD, remove the top cover to expose the vent-valve.
5.2.2.6 Turn off the main power switch to the MSD and release the vacuum from the vent-valve. Disconnect the main power supply if service to the MSD is intended.
5.2.2.7 Shut off the helium flow to the GC and turn off the GC main power if necessary.
5.2.2.8 For the 5971/5972 MSD, release the vacuum by removing the GC column from the detector side.

5.3 Instrument Maintenance

See Agilent Technologies 5973 Network MSD Hardware Manual Chapter 6 Maintaining the MSD
5972 Manual Chapter 4
5971 Manual Chapter 6

All instrument maintenance shall be recorded in the instrument's logbook.

5.3.1 Mass Spectrometer

5.3.1.1 Checking and changing fore-pump oil:
5973 Manual pp. 160 -155
5972A Manual pp. 168 - 173
5971A Manual pp. 6-14 - 6-19

5.3.1.1.1 Oil level shall be checked at least once a week.
5.3.1.1.2 Pump oil shall be changed every 4-6 months depending on usage or according to the specification of the method's SOP.

5.3.1.2 Cleaning Ion Source
(Refer to 5973 Manual pp. 206-221, pp. 230-231,
5972A Manual pp. 202 - 227;
5971A Manual pp. 6-41 - 6-58.)

5.3.1.2.1 The ion source shall be cleaned every 4-6 months depending on usage or according to the specification of the method's SOP.
5.3.1.2.2 Follow the Agilent Technologies MSD Hardware Manual to perform ion source maintenance.
5.3.1.2.3 Replacing Electron Multiplier
Replace according to the specification of the method or as needed.

5.3.2 Gas Chromatography

5.3.2.1 Replacing Inlet liner and O-ring:
Replace according to the specification of the method, or as needed
5.3.2.2 Replacing Inlet end-disk and gasket:
Replace according to the specification of the method.
5.3.2.3 Replacing column and pre-column:
Replace according to the specification of the method
5.3.2.4 To replace and condition a GC column, follow the instructions in Agilent Technologies 5973 Network MSD Hardware Manual pp. 20-31.
5972A Manual, p. 18
5971A Manual, p. 4

5.3.3 Maintaining the GC/MSD Interface (5972 & 5971 MSD)
5971A Manual pp. 6-64

5972A Manual pp. 229 - 237

5.4 Instrument Troubleshooting

See Agilent Technologies 5973 Network MSD Hardware Manual Chapter 4 Troubleshooting the MSD and Chapter 5 CI Troubleshooting.
5972A MSD Manual Chapter 3, p. 63
5971A MSD Manual Chapter 5, p. A-31

6. References:

Agilent Technologies 5973 Network Hardware Manual
Agilent /HP 5972A MSD Hardware Manual
Agilent /HP 5971 MSD Hardware Manual

7. Comments:

All of the procedures described above are based on the Agilent Technologies 5973 Network Hardware Manual for instructions.

The software is revised periodically. If the steps in the Agilent Technologies 5973 Network Hardware Manual do not match your MS ChemStation software, refer to the manuals and online help supplied with the software for more information.

Reviewed By:

_____ _____
Terry Jackson Date
Quality Assurance Officer

Approved By:

_____ _____
William Cusick Date
Branch Chief

Revision Log:

Date	Revision #	Reasons for Deviation	Approved By	Date